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Photovoltaic Investigations Utilizing Stannic Oxide Single Crystals

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PHOTOVOLTAIC INVESTIGATIONS UTILIZING

STANNIC OXIDE SINGLE CRYSTALS

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Date

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INTRODUCTION

The energy crisis of the 1970's led to a considerable research effort in typical p-n junctions used in solar cells. However, there are several other types of photovoltaic effects worthy of investigation. Two of these effects are of particular interest to this study.

One of these is the Dember photovoltaic effect. This effect occurs in the bulk of the semiconductor and arises from the differences in hole and electron mobilities. It requires a semiconductor with metal contacts exposed to light which is nonuniformly distributed.

A second type of photovoltaic effect of particular interest is that which occurs in Schottky-barrier devices. These devices are created from direct contact between a metal and a semiconductor. Recently several investigators have reported photovoltaic effects in Schottky-barrier devices and analyzed their behavior.

During this investigation a previously unreported photovoltaic effect was observed for stannic oxide (SnO_2) single crystals. The primary objective of this investigation is to verify the reproducibility of this effect and to determine the extent to which the above mentioned theories explain the observed photovoltage.

OBJECTIVES

Specific objectives of this investigation were:

1. To verify the existence of a photovoltaic effect for stannic oxide single crystals with platinum contacts.
2. To study the effect of the surface potential barrier of stannic oxide on the photovoltaic effect. Variation of the barrier is accomplished by heat treatments in oxygen and nitrogen environments.
3. To understand the role of the metal contacts in the production of the photovoltage.

BACKGROUND LITERATURE

The semiconductor material of primary interest to this investigation is stannic oxide (SnO_2). It is the main constituent in natural tin ore.[18] In its natural crystalline form it is called cassiterite. The symmetry of the SnO_2 crystal is equivalent to that of the more well known rutile (TiO_2).[40] The unit cell of a single crystal of SnO_2 is shown in Figure 1.

Stannic oxide in its pure form is an n-type metal oxide semiconductor. Its electrical conduction results from the existence of point defects (oxygen vacancies and interstitial tin atoms) which act as donors.[27] Several investigations of both optical and electrical properties of SnO_2 have been reported.[21] Miloslavskii[23] obtained activation energies of 0.12 eV from conductivity data in the temperature range of 150°C to 200°C, and electron densities of 10^{19} to 10^{20} cm^{-3} for thin films of natural SnO_2. Khonke[15] reports values of 0.72 eV for other natural crystalline samples of SnO_2 and electron densities of 10^{14} to 10^{15} cm^{-3} at room temperature. Further, he reports a direct band gap of 3.54 eV from the short wavelength cutoff in transmission data. This value can be compared to a value of 3.44 eV obtained by Hurt and Khonke,[14] from the maximum of the photoconductivity spectral response data. Samples grown in a cuprous oxide flux were found to have much smaller electron densities and displayed a direct energy gap of about 4.0 eV.[12]

The initial stages of this investigation involved extensive study of the Dember photovoltaic effect. This effect is named after

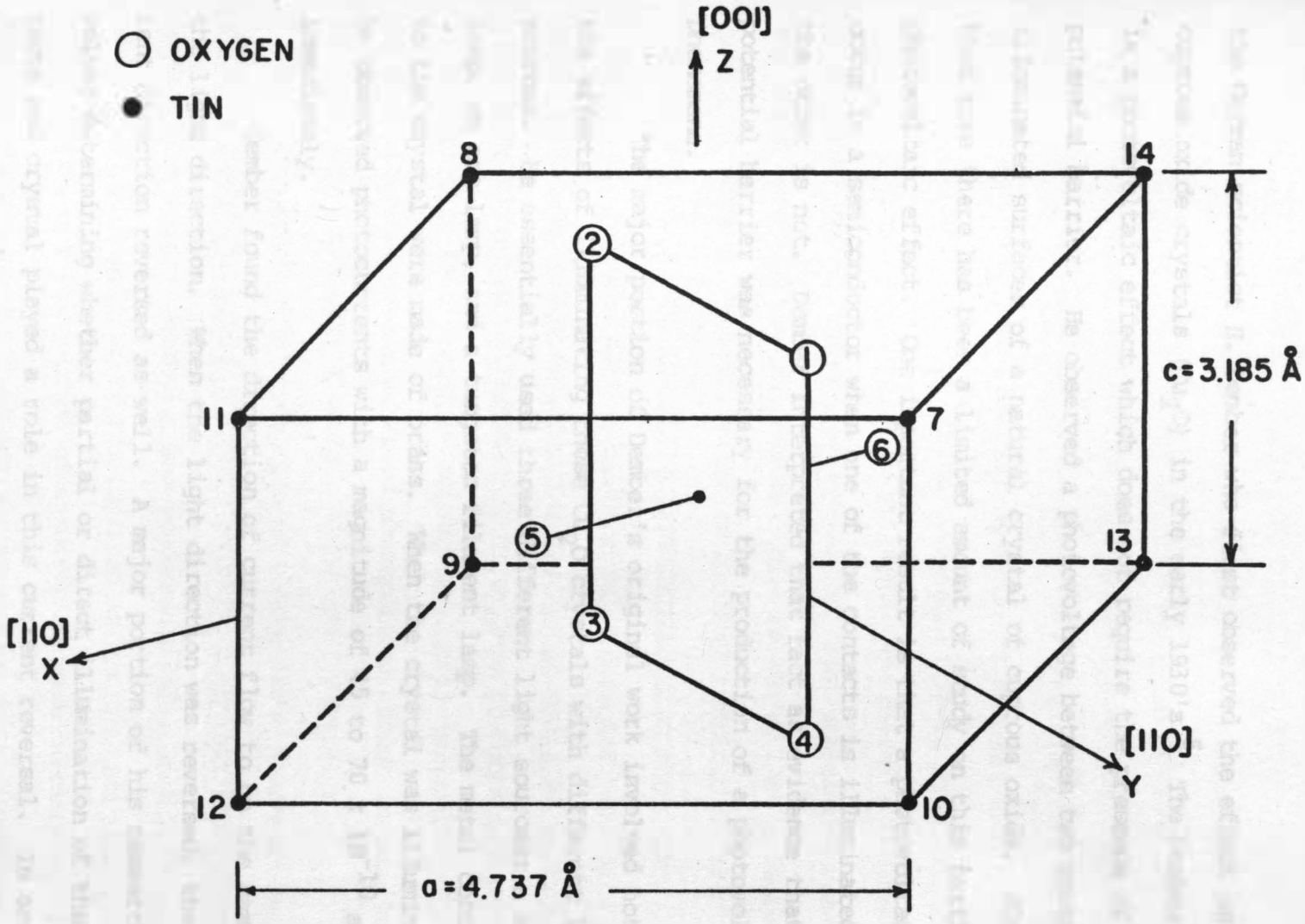


Figure 1. The Unit Cell of SnO_2

the German scientist H. Dember who first observed the effect using cuprous oxide crystals (Cu_2O) in the early 1930's.[5] The Dember effect is a photovoltaic effect which does not require the presence of a potential barrier. He observed a photovoltage between two unequally illuminated surfaces of a natural crystal of cuprous oxide. Since that time there has been a limited amount of study on this particular photovoltaic effect. One important result is that a photovoltage can occur in a semiconductor when one of the contacts is illuminated and the other is not. Dember interpreted that fact as evidence that no potential barrier was necessary for the production of a photovoltaic phenomena.

The major portion of Dember's original work involved noting the effects of illuminating these Cu_2O crystals with different light sources. He essentially used three different light sources: a mercury lamp, an arc lamp, and a tungsten filament lamp. The metal contacts to the crystal were made of brass. When the crystal was illuminated he observed photocurrents with a magnitude of 45 to 70 x 10^{-10} amperes immediately.

Dember found the direction of current flow to be the same as the light direction. When the light direction was reversed, the current direction reversed as well. A major portion of his research involved determining whether partial or direct illumination of the contacts and crystal played a role in this current reversal. In order to do this he mounted the crystal so that it could be rotated such that the light could be positioned at various points on the crystal.

After some further investigations, Dember concluded that the light direction plays an essential role in the production of the observed photovoltaic effect. He also observed that the creation of an emf inside the crystal can be produced only when the light is capable of freeing electrons so that they are able to diffuse inside the crystal. He further observed that the electron concentration is changed by light absorption along the light path. The electron concentration is a maximum at the entrance point of the light and then decreases in the light direction in proportion to the amount of light absorbed in each unit volume. The concentration gradient produced in this way then drives the electrons in the same direction as the light. Finally, he concluded that this observation does not exclude a possible contribution due to a barrier layer. However, he felt this barrier layer alone was not sufficient to explain the observed phenomena. This leads to a very important aspect of this investigation. That is, to determine whether the observed photovoltaic effect in SnO_2 is a barrier layer or a bulk effect.

The present-day conception of photovoltaic phenomena begins with the theory proposed by Mott[24] in 1939 to explain the function of the cuprous oxide photocell. The fundamental idea of this theory is that a potential barrier exists in a semiconductor, the electric field of which prevents the passage of majority current carriers but permits the passage of minority carriers to the metal. Mott's original work was done with a cuprous oxide semiconductor with copper contacts (Cu_2O-Cu). In this case the majority carriers in Cu_2O are the holes,

which have a p-type conductivity, and the minority carriers are the electrons. Mott's fundamental ideas are used in a number of detailed theories of various photovoltaic phenomena elaborated on by several authors.

There has been no extensive research on the Dember effect since Dember reported his original results. Investigators that have studied the Dember effect have found changes in Dember's original theory. In his work dealing with poor electronic conductors in 1933, Frenkel[6] concluded that the potential difference generated with strong light absorption was due to the Dember effect.

Previously, Dember had concluded that the presence of a barrier layer is not essential in establishing a photovoltaic effect. Later investigators tend toward the idea that a photovoltage can be detected if the semiconductor is in some way nonhomogenous. The results of work done by Tauc[37] shows that a photovoltage can be produced in a semiconductor if the semiconductor is nonhomogenous in the sense that its conductivity changes over its length. He found that if this change in conductivity occurs at distances smaller than the Debye length of the semiconductor, then potential barriers are produced and Mott's general theory holds. Further work done by Tauc[38] shows that a photovoltage can be produced even when the change in conductivity is so gradual that the junctions are neutral. This is contrary to Mott's general theory since his theory requires space charges and strong electric fields. Tauc concluded that if neither localized barriers nor contacts take part in the production of a photovoltaic

effect it is then termed a bulk photovoltaic effect. Tauc further concluded that a non-rectifying metal semiconductor contact is essential for the Dember photovoltaic effect to be observed. However, he makes no reference to the generation of an emf at the contacts between a metal and a semiconductor because the structure of the contacts is quite complicated and not completely understood.

Ostrowski[29] studied the effect of space charge on the Dember effect in a superficially illuminated semiconductor sample. To carry out his investigations he assumed that the incident light generates electron-hole pairs (EHP) at the surface of the semiconductor only. That is, the light penetration depth equals zero. In addition to surface generation, a surface recombination is allowed, so that only a fraction of the created carriers actually penetrate the semiconductor. He also assumed that the sample thickness is much greater than the diffusion length, L_D. Thus, in the limit that the sample thickness approaches infinity, the concentration of excess carriers, Δn and Δp, can be taken as approaching zero values.

For the steady-state case, Ostrowski found that the Dember voltage calculated with space charge taken into account is smaller than that using the neutrality theory. According to the neutrality theory, the Dember voltage appears the moment the sample is illuminated. Finally, Ostrowski concluded that there was a marked influence of space charge upon the Dember effect, which he found to be the most pronounced during time dependent processes.

Goldman, et al[9] investigated photovoltages produced in CdS-type insulated crystals excited by strongly absorbed radiation. He states that the effects of a photovoltage are somewhat lessened when the electrodes are connected directly to the semiconducting crystal because of the charge injection introduced. He found that the Dember voltage is best observed when the crystal is insulated from the electrodes at both sides. Further, he felt that the insulation may very simply be the presence of chemisorbed oxygen at the surface of the semiconductor.

In addition, Goldman states that the concentration of free electrons at the illuminated side of the sample is lowered due to thermal diffusion. It is this lowered concentration of free electrons that results in the creation of an excess positive charge at the illuminated edge and is the cause of the Dember photovoltage.

Patterson[31] indicates that if an n-type semiconductor with ohmic contacts is partially illuminated so that the radiation falls on one half of the specimen, the photovoltage that may develop at the illuminated edge may be of such a direction and magnitude so as to nearly cancel out the Dember effect. In making this observation he assumed that the semiconductor had no space charge, that the excess electron concentration in the metal is controlled by a single carrier diffusion equation, and that the sample is sufficiently thin to make the problem one dimensional. These assumptions tend to be an oversimplification of the problem.

Scott and Reed[33] indicate that for the case of highly sensitive photoconductors the Dember voltage may reach several hundred millivolts. However, with less sensitive photoconductors they indicate that the excess carrier concentrations are seldom large enough to give a Dember potential in excess of a few millivolts.

These investigators modulated the incident radiation and detected the resulting AC voltage at the electrode. They define the surface photovoltage as the change in surface barrier height produced by intense illumination of the free semiconductor surface. An electrometer connected to a stationary transparent electrode was used to measure the potential change at the surface upon illumination. For weak illumination intensities, they concluded that the Dember photovoltage is unlikely to be produced.

Han and Anderson[11] use the generation of the Dember field to explain the difference in open circuit voltage between N-I-P and P-I-N amorphous silicon hydride solar cells. They found that the Dember field aids carrier collection in N-I-P cells but opposes carrier collection in P-I-N cells.

Takagi and Kawabe[36] report a significant photovoltage detected in single crystals of an organic semiconductor 1,1'-diethyl-2,2'-quinocyanine $(TCNQ)_2$. The photovoltage was observed when the crystal was nonuniformly illuminated and was attributed to the Dember potential.

Dalal and Rothwarf[4] discuss the effects of the Dember field on measurements of solar cell quantum efficiency. The cells used were

made of a Cds/Cu_2S type material. They found that as the intensity of light increases, electron-hole plasma tends to build up in the base layer. When the density of this plasma becomes comparable to the background density, the Dember field, which is due to a difference in electron and hole mobilities, tends to influence the quantum efficiency. For example, the mobility of electrons in silicon is greater than that of holes. Thus, the electron "cloud" diffuses further into the crystal than the hole cloud. The net results is that the photogenerated electrons encounter a "sea of electrons" in the base layer which tends to repel the diffusing electrons away from the junction. Alternately, the holes that are generated in the base layer are attracted towards the junction.

As the present investigation progressed, it was found that the Dember effect did not totally explain the observed photovoltage. Thus, a study of photovoltaic effects in Schottky-barrier diodes was undertaken to help understand the observed effect.

According to Williams[41] the exact mechanisms that govern the formation of Schottky barriers at the interface between metal and semiconductor are not completely understood. Thus continued study is necessary to help understand the particular mechanisms. The investigation becomes even more complicated when dealing with Schottky-barrier photovoltaic effects.

Ghosh, et al[8] worked with SnO_2/Si solar cells as photovoltaic devices. The devices consisted of a junction between two semiconducting materials, SnO_2 and Si. It performs like a metal-

insulator-semiconductor device (MIS). In the limit that the oxide layer is very thin, it also performs as a Schottky-barrier device. These SnO_2/Si solar cells were made by depositing SnO_2 onto a single crystal Si substrate using an electron beam. This is done employing a low-temperature process in an effort to reduce degradation of carrier lifetimes. The barrier is located at the SnO_2/Si interface which could result in reduced surface recombination and result in large short-circuit photocurrents. Further, it is possible for a thin layer of SiO_2 to form at the interface during processing. This oxide layer can affect the performance of the device.

For the short-circuit photocurrent it is assumed that the electrons from the SnO_2 tunnel through the oxide layer at the interface and recombine with the light-generated holes. If the oxide layer were too thick, then the light-generated holes may recombine with electrons in the Si which gives rise to a loss in photocurrent.

Finally, these investigators conclude that if surface states do not interfere, the maximum open-circuit voltage is related to the difference in the work function between SnO_2 and Si. However, it is also reported that an interfacial insulating layer may affect the diffusion potential as well as the magnitude of the open-circuit photovoltage.

Further investigation of the role of the interfacial layer in Schottky-barrier solar cells has been undertaken by Swami, et al[35]. They have found that the interfacial layer is instrumental in reducing the dark current, which tends to increase the open-circuit voltage and

the efficiency of the solar cell. This is important because Schottky-barrier solar cells usually have a lower open-circuit voltage than ordinary p-n junction solar cells.

Further, these investigators imply that the interfacial layer plays an important role in determining the short-circuit current, open-circuit voltage, and efficiency of the cell. However, the exact role of the interfacial layer is not completely understood.

Lue[20] reports on the change in barrier height and current transport phenomena with the presence of an interfacial layer in MIS Schottky-barrier solar cells. He found that when the dark current is reduced the net result is an increase in the open-circuit voltage. This fact is further supported in the theory proposed by Klimpke[16]. Further, when the positive ions are introduced into the insulating layer, the barrier height decreases for n-type and increases for p-type semiconductors. Finally, an increase in open-circuit voltage is also attributed to the decrease in tunneling by majority carriers because of the presence of an oxide potential barrier.

Gutkowicz-Krusin[10] studied the effects of recombination on the carrier collection efficiency of amorphous silicon hydride Schottky-barrier solar cells. In her investigation she determined the dependence of the collection efficiency on the nature of the contacts, the film thickness, the hole diffusion length, the absorption length, and the width of the depletion region. Further, she assumed direct metal-semiconductor contact with no insulating layer. She found the

drift carriers dominated the diffusion current since the electric field acting on the carriers is large for narrow depletion regions.

The thickness of the film also plays an important role in determining carrier collection efficiencies. For thick films, a large fraction of the carriers are generated outside the depletion region. This is also the region of weak electric fields. The net result is a large probability of recombination before the carriers are collected. Gutkowicz-Krusin found that there is an optimal thickness for maximizing the efficiencies of solar cells.

Further results determined by Mottram, et al[25] have not shown any type of simple correlation between the work function changes caused by oxygen adsorption and the corresponding barrier height changes caused by the presence of oxygen at the interface. Garner, et al[7] states that the electrical behavior of Schottky-barriers is affected by the presence of an oxide layer. However, little is known about the effect of the composition of the oxide layer on the electrical characteristics in the Schottky-barrier photovoltaic cell. Thus, it is part of the scope of the present investigation to help explain the role of this oxide layer in SnO_2.

SEMICONDUCTOR AND PHOTOVOLTAIC EFFECT THEORIES

Photovoltaic p-n Junction Theory

In order to describe the creation of a photovoltage by a p-n junction, a discussion of semiconductor band theory and its relationship to the p-n junction is appropriate.

The energy spectrum of electrons in a semiconductor is composed of continuous bands. This differs from that of atoms or molecules, in which the energy spectrum is a set of discrete levels. The regions separating these bands are called energy gaps. The energy gaps are regions of forbidden energy in which no electron can exist. This is shown schematically in Figure 2.

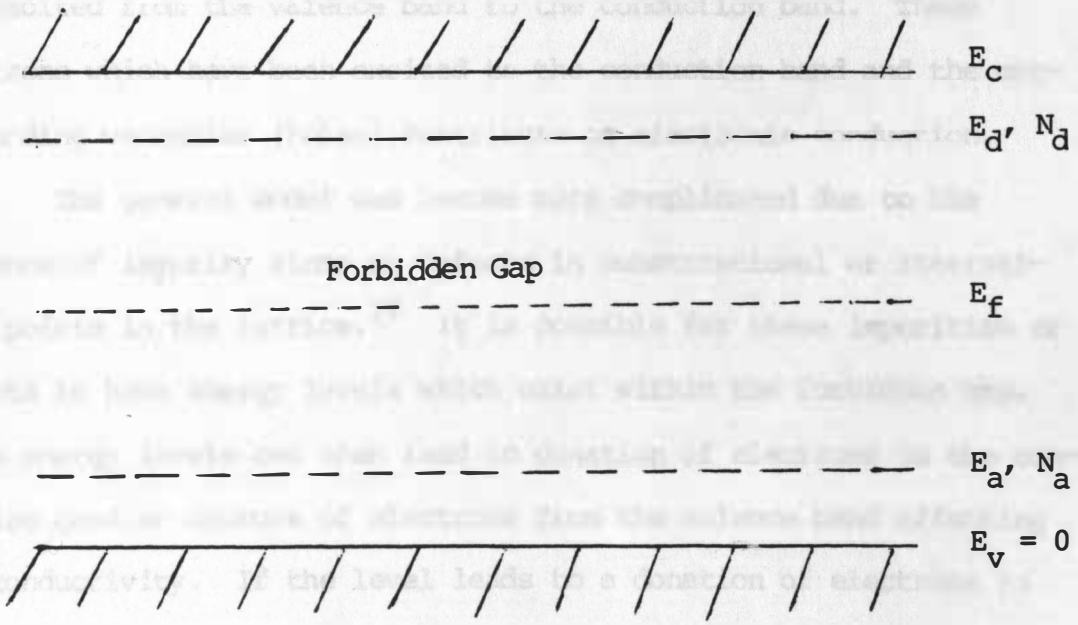


Figure 2. Semiconductor Band Model

where: N_d = density of donor states

E_d = activation energy of donor states

E_f = position of Fermi level

N_a = density of acceptor states

E_a = activation energy of acceptor states

E_c = energy of the bottom of the conduction band

E_v = arbitrary zero and energy of the top of the valence band

The general model assumes that at absolute zero, all the electrons are in the valence band at or below energy $E_v = 0$. The band immediately above the valence band is the conduction band and it is totally void of electrons. A forbidden gap exists between these two bands. As the temperature of the semiconductor is raised, electrons are excited from the valence band to the conduction band. These electrons which have been excited to the conduction band and the corresponding vacancies (holes) contribute to electronic conduction.

The general model can become more complicated due to the presence of impurity atoms or defects in substitutional or interstitial points in the lattice.[17] It is possible for these impurities or defects to have energy levels which exist within the forbidden gap. These energy levels can then lead to donation of electrons to the conduction band or capture of electrons from the valence band affecting the conductivity. If the level leads to a donation of electrons to the conduction band it is called a donor level and is described by N_d and E_d. Levels which lead to a capture of electrons from the valence band are called acceptor levels and are described by N_a and E_a. An

n-type semiconductor is one in which donor levels dominate the conduction process with electrons being the charge carriers. Conversely, a p-type semiconductor is one dominated by acceptor levels and thus holes are the dominant charge carriers.

When n-type and p-type materials are joined as shown in Figure 3a, electrons diffuse into the p-region and holes diffuse into the n-region. This leads to the formation of a space charge or depletion region as shown. The energies of electrons in the n-region are lowered by this charge distribution and those in the p-region are raised by an equal amount. Thus the potential hill is formed at the junction as shown in Figure 3b.

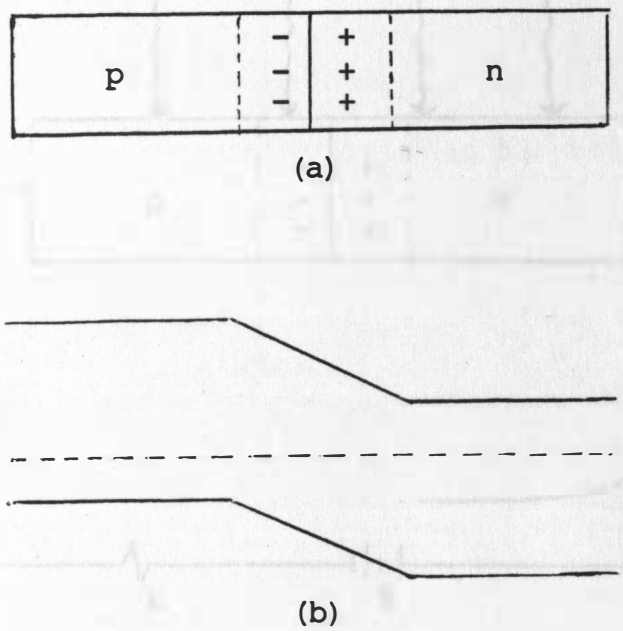


Figure 3. (a) The p-n Junction and,
(b) the Corresponding Band Diagram

In order to describe the response of p-n junctions to the optical generation of electron-hole pairs, the generation current should be defined. The generation current is the current which occurs due to the drift of minority carriers across a junction driven by the electric field created by the depletion region. This generation current is balanced by an equal and opposite diffusion current when the junction is in equilibrium. However, when the junction is illuminated by photons with energies greater than band gap ($h\nu > E_g$), the number of minority carriers is increased leading to an increased generation current and thus a net current flow as shown in Figure 4.

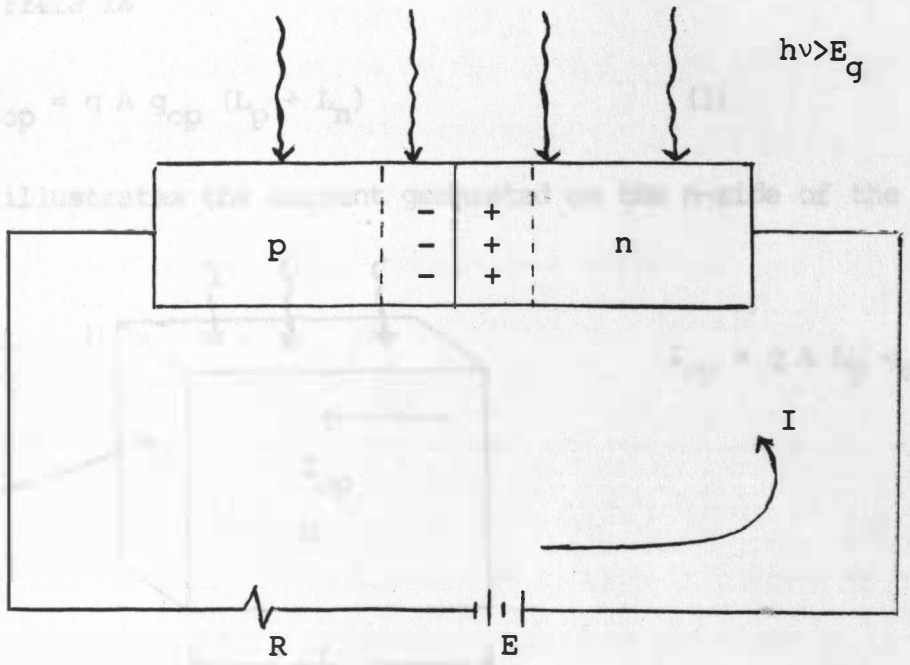


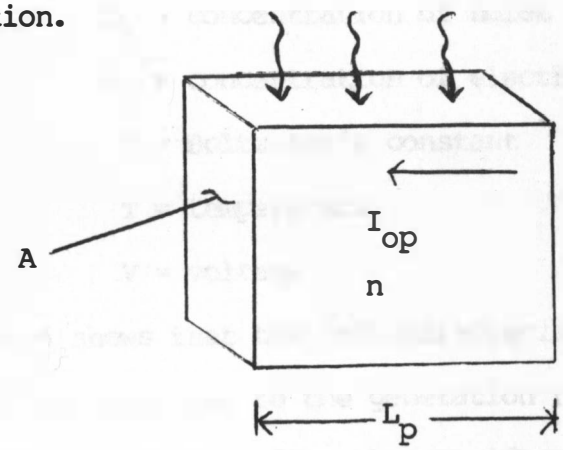
Figure 4. Optical Generation of Carriers in a p-n Junction; Absorption of Light by the Device

The generation rate of minority carriers is designated by g_{op} (EHP/cm^3-sec). An assumption is generally made that only carriers generated within one diffusion length of the junction are effective in producing the generation current since carriers outside of this region have only small probability of reaching the junction before recombination takes place.

There are $AL_p g_{op}$ holes generated per second within a diffusion length (L_p) of the transition region on the n-side. Similarly, $AL_n g_{op}$ electrons are generated per second within a diffusion length (L_n) of the transition region on the p-side. The current that results from these minority carriers being swept across the junction by the electric field is

$$I_{op} = q\, A\, g_{op}\, (L_p + L_n) \qquad (1)$$

Figure 5 illustrates the current generated on the n-side of the junction.



$$I_{op} = q\, A\, L_p\, g_{op}$$

Figure 5. Current I_{op} Resulting from EHP Generation Within a Diffusion Length of the Junction on the n-side

The current of equation 1 subtracts from the total current from p to n since it is directed from the n to the p region. The usual diode equation[34] is

$$I = qA \left(\frac{D_p}{L_p} p_n + \frac{D_n}{L_n} n_p\right)(e^{qV/kT} - 1) \qquad (2)$$

Equation 2 must be modified for an illuminated diode. The resulting current-voltage relationship for an illuminated diode is then,

$$I = qA \left(\frac{L_p}{\tau_p} p_n + \frac{L_n}{\tau_n} n_p\right)(e^{qV/kT} - 1) - qA\, g_{op}(L_p + L_n) \qquad (3)$$

where: q = charge of an electron

A = area of junction

L_p, L_n = diffusion lengths in the n- and p- regions respectively

τ = lifetime of a free carrier

D_p, D_n = diffusion constants

p_n = concentration of holes in n-region

n_p = concentration of electrons in p-region

k = Boltzmann's constant

T = temperature

V = voltage

Figure 6 shows that the I-V characteristic curve is lowered by an amount proportional to the generation rate when the diode is illuminated. Equation 3 may be considered in two parts: (1) the current described by the usual diode equation (equation 2), and, (2) the current due to the optical generation.

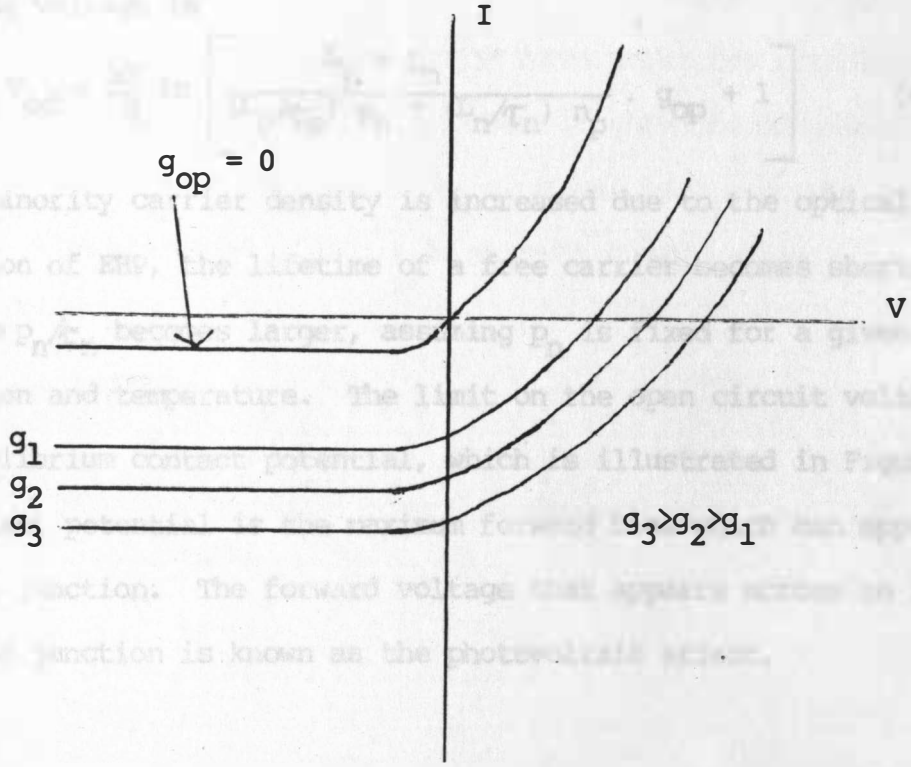


Figure 6. I-V Characteristics of an Illuminated Diode

When the device is short-circuited (V=0), the I-V characteristics of Figure 6 cross the I-axis at negative values. This occurs because the thermal generation, injection, and recombination currents cancel in equation 3. Further, there is a resulting short-circuit current from n to p equal to I_{op} which is proportional to g_{op}.

When there is an open circuit (I=0) across the device, the resulting voltage is

$$V_{oc} = \frac{kT}{q} \ln \left[\frac{L_p + L_n}{(L_p/\tau_p)\, p_n + (L_n/\tau_n)\, n_p} \cdot g_{op} + 1 \right] \qquad (4)$$

As the minority carrier density is increased due to the optical generation of EHP, the lifetime of a free carrier becomes shorter, and the term p_n/τ_n becomes larger, assuming p_n is fixed for a given concentration and temperature. The limit on the open circuit voltage is the equilibrium contact potential, which is illustrated in Figure 7. The contact potential is the maximum forward bias which can appear across a junction. The forward voltage that appears across an illuminated junction is known as the photovoltaic effect.

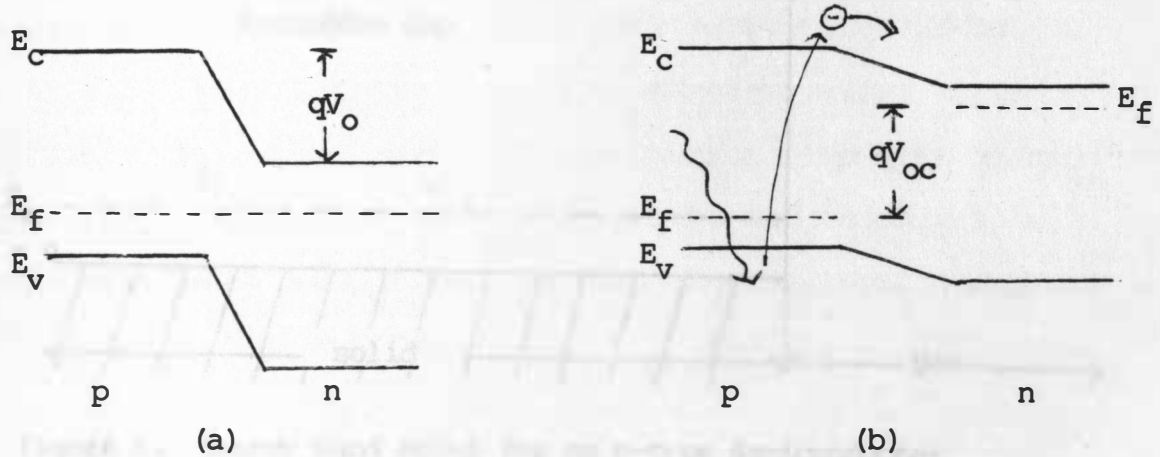


Figure 7. Effect of Illumination on the Open-circuit Voltage of a Junction: (a) Junction at Equilibrium, (b) Appearance of a Voltage V_{oc} with Illumination

Semiconductor Surface Theory

The general model to be used in this investigation assumes that the samples are compensated n-type semiconductors with surface acceptor states arising from the presence of chemisorbed oxygen.[22] Chemisorbed atoms or molecules form a chemical bond with the solid's surface. Figure 8 shows a simple band model of an n-type semiconductor.

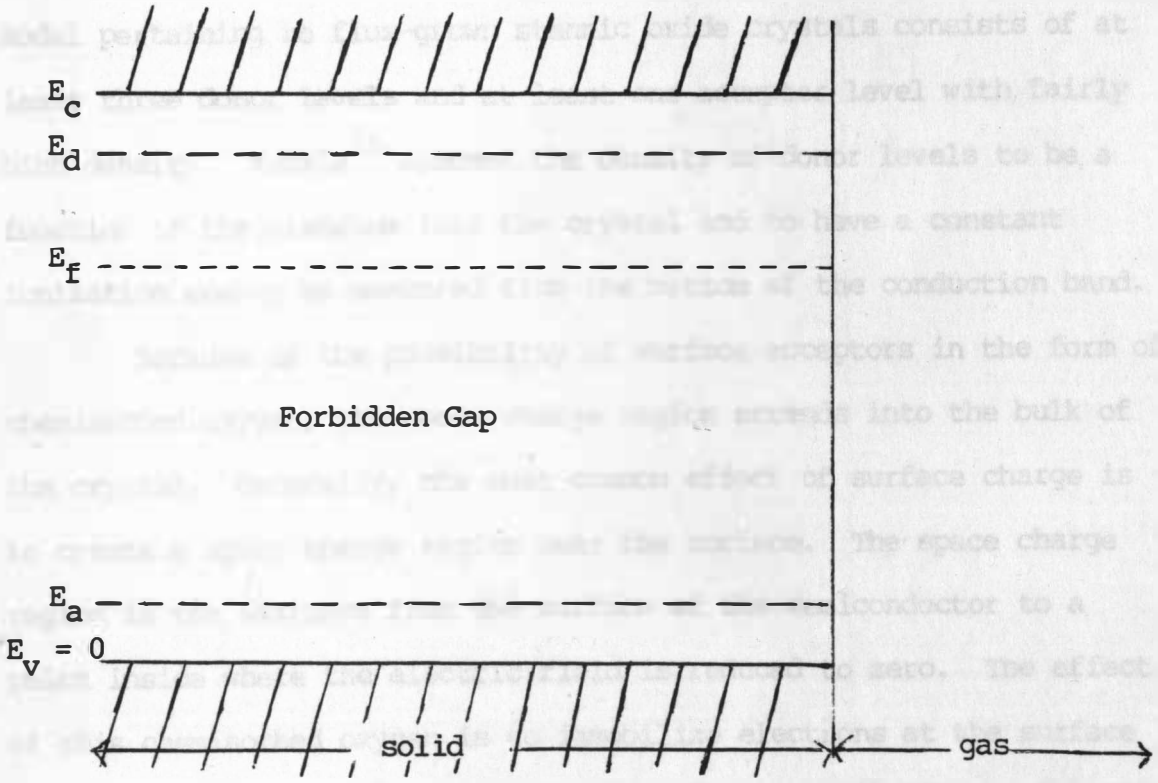


Figure 8. Energy Band Model for an n-type Semiconductor

The effect of the surface on a semiconductor is extremely important in understanding the mechanism involved with the observed

photovoltaic effect. It is at the surface that the particular semiconductor material may react chemically with its surroundings. Further, it is at the surface that a discontinuity in the lattice potential occurs causing an upward bending of the energy bands at the semiconductor-gas interface. The states that arise due to this discontinuity can be called intrinsic states.

Of particular interest to this investigation is the effect of oxygen and nitrogen at the surface of the semiconductor. The general model pertaining to flux-grown stannic oxide crystals consists of at least three donor levels and at least one acceptor level with fairly high density. Kunkle[18] assumed the density of donor levels to be a function of the distance into the crystal and to have a constant ionization energy as measured from the bottom of the conduction band.

Because of the possibility of surface acceptors in the form of chemisorbed oxygen, the space charge region extends into the bulk of the crystal. Generally, the most common effect of surface charge is to create a space charge region near the surface. The space charge region is the distance from the surface of the semiconductor to a point inside where the electric field is reduced to zero. The effect of this chemisorbed oxygen is to immobilize electrons at the surface of the semiconductor which prevents them from contributing to the conduction process.

Rutledge's model[32] is applicable to heavily compensated semiconductors (i.e. $n<N_a<N_d$, where n is the concentration of electrons) upon which chemisorbed gas states exist as filled acceptor levels.

Matthews[22] and Rutledge[32] propose that oxygen is the active component for SnO_2 forming acceptor centers upon chemisorption. Figure 9 shows the effect of chemisorbed oxygen at the surface of the semiconductor. It illustrates the adsorption of an oxygen ion onto the surface of the semiconductor and the trapping of conduction band electrons. This mechanism decreases the number of available electrons in the conduction band and thus decreases the electronic conductivity.

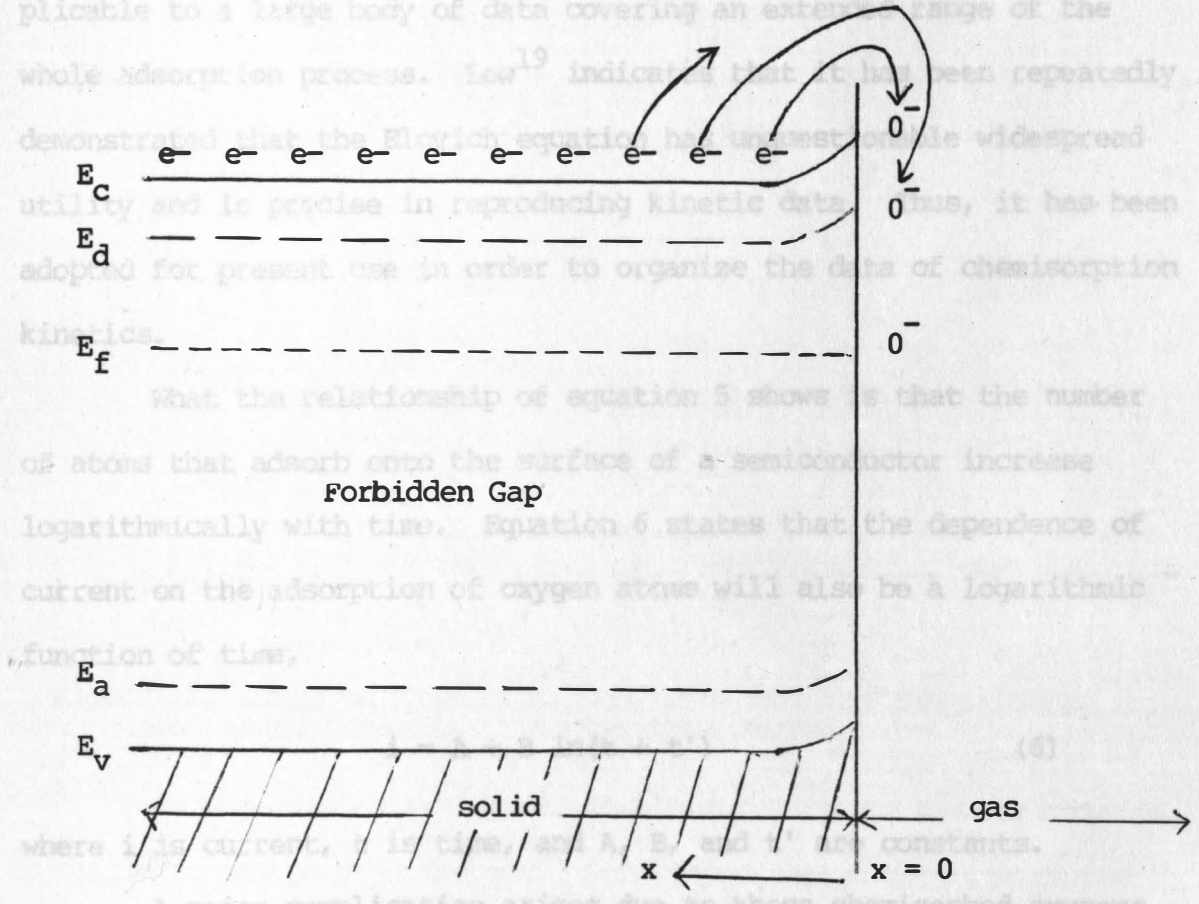


Figure 9. Effect of Oxygen Adsorption on Conduction Band Electrons

Matthews[22] and Rutledge[32] have found the chemisorption process follows the Elovich rate law

$$N = A \ln(t + t') \tag{5}$$

where N is the number of molecules adsorbed, t is time and A and t' are constants which depend on temperature and number of atoms involved. Taylor and Thon[39] have determined that this equation is applicable to a large body of data covering an extended range of the whole adsorption process. Low[19] indicates that it has been repeatedly demonstrated that the Elovich equation has unquestionable widespread utility and is precise in reproducing kinetic data. Thus, it has been adopted for present use in order to organize the data of chemisorption kinetics.

What the relationship of equation 5 shows is that the number of atoms that adsorb onto the surface of a semiconductor increase logarithmically with time. Equation 6 states that the dependence of current on the adsorption of oxygen atoms will also be a logarithmic function of time,

$$i = A + B \ln(t + t') \tag{6}$$

where i is current, t is time, and A, B, and t' are constants.

A major complication arises due to these chemisorbed oxygens. It is the bending of the energy bands near the surface of the sample as illustrated in Figure 10. The bending of the energy bands causes the potential barrier to increase. Now each electron must acquire

even more energy to overcome the potential barrier. This leads to an increase in contact resistance. Since the process lowers the Fermi level, a decrease in bulk conductivity is also observed. The location of the surface states are not specifically shown on Figure 10 because their positions are not completely understood.

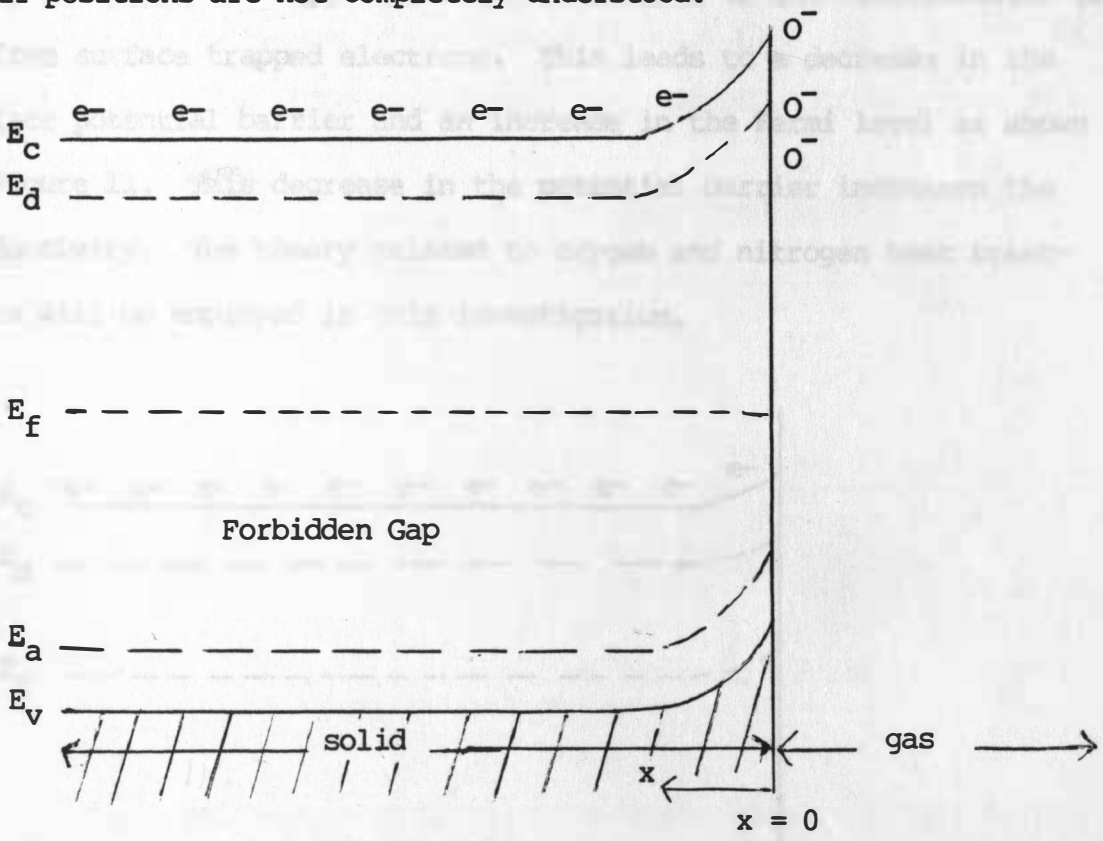


Figure 10. Modified Band Model Due to Surface Acceptor States Caused by the Presence of Chemisorbed Oxygen

An opposite effect occurs when the crystal is heat treated in a nitrogen atmosphere. Tunheim[40] postulated that oxygen leaves the crystal during the treatment in nitrogen and thus it can be termed a reducing atmosphere. As the oxygen ions leave the surface of the crystal they release one or two electrons for each ion involved. The net effect is to raise the Fermi level closer to the conduction band.

Tunheim substantiated his proposed model by showing that the crystal gained weight when treated in an oxygen atmosphere and lost weight when treated in a nitrogen atmosphere. He has also shown that this change in weight is reversible.

A result of oxygen leaving the surface of the semiconductor is to free surface trapped electrons. This leads to a decrease in the surface potential barrier and an increase in the Fermi level as shown in Figure 11. This decrease in the potential barrier increases the conductivity. The theory related to oxygen and nitrogen heat treatments will be employed in this investigation.

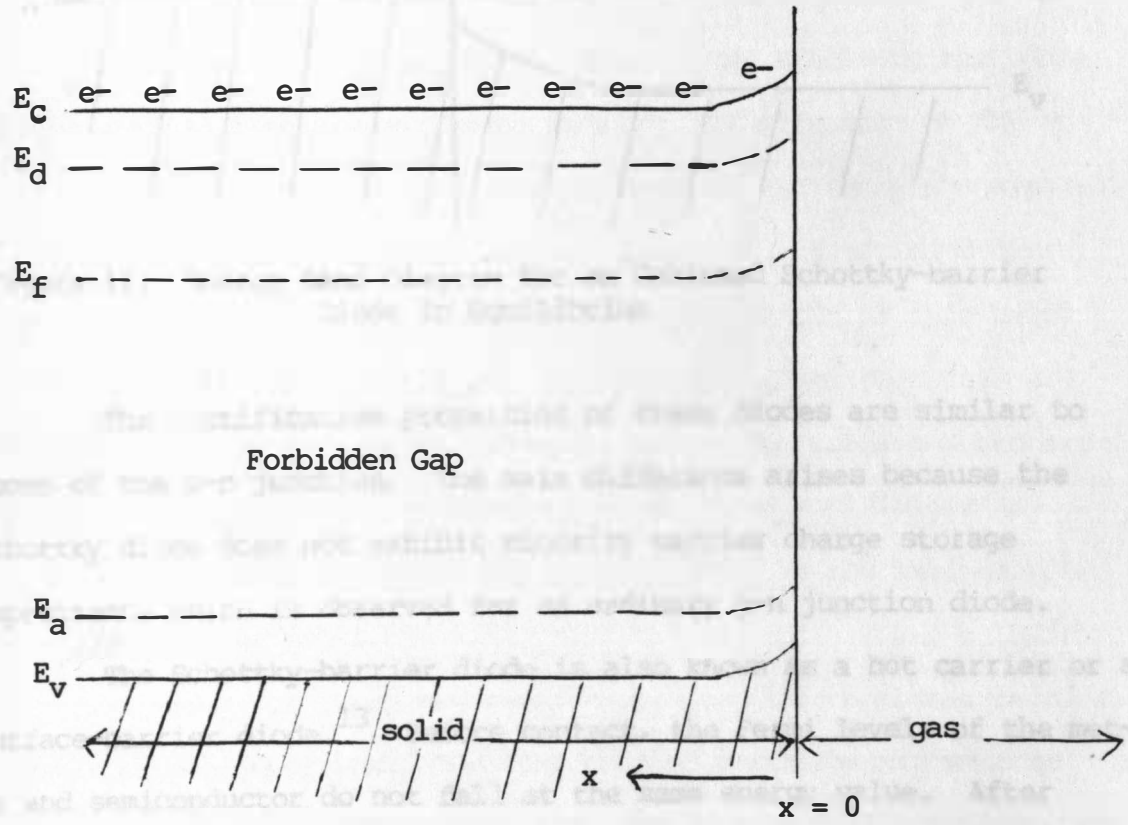


Figure 11. Modified Band Model for Heat-treatment in a Nitrogen Atmosphere

Schottky Photovoltaic Effect Theory

Schottky-barrier diodes are also known as metal semiconductor diodes. They are based on the rectifying properties of the Schottky barrier. Figure 12 shows the behavior of the energy bands for a Schottky-barrier diode in the unbiased state. The work function, ϕ_B, is defined as the height of the energy barrier at the surface.[28] This function varies for different metals, but generally falls within the range 1.5 - 5.0 eV.

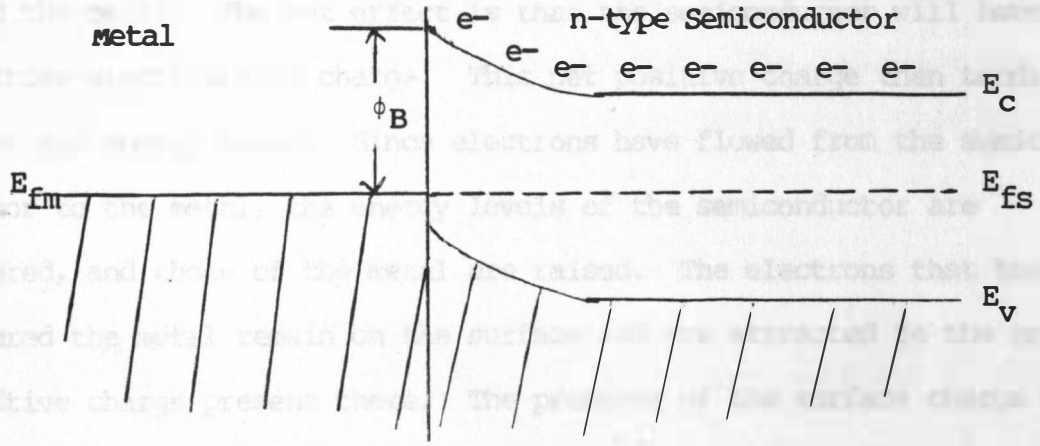


Figure 12. Energy Band Diagram for an Unbiased Schottky-barrier Diode in Equilibrium

The rectification properties of these diodes are similar to those of the p-n junction. The main difference arises because the Schottky diode does not exhibit minority carrier charge storage capacitance which is observed for an ordinary p-n junction diode.

The Schottky-barrier diode is also known as a hot carrier or a surface-barrier diode.[13] Before contact, the Fermi levels of the metal and semiconductor do not fall at the same energy value. After contact is made between the two materials they become a single

thermodynamic system. There must then be a single Fermi level for the system.

Before contact, the free electrons in the semiconductor are generally at higher levels of energy than in the metal. This follows directly from the fact that the Fermi level in the semiconductor is higher than in the metal. When an electrical contact is made, the higher energy electrons will tend to lower their energy by flowing into the metal. The net effect is that the semiconductor will have a positive electrostatic charge. This net positive charge then tends to lower the energy bands. Since electrons have flowed from the semiconductor to the metal, the energy levels of the semiconductor are lowered, and those of the metal are raised. The electrons that have entered the metal remain on the surface and are attracted to the net positive charge present there. The presence of the surface charge of electrons in the metal and the ionized donors of the semiconductor form the potential barrier after contact. The height of this barrier is determined by how much the energy bands of the semiconductor are lowered and how much those of the metal are raised after the electrons flow into the metal. The electrons flow until an equilibrium is reached and the Fermi level of the semiconductor is the same as the Fermi level of the metal.

Photovoltaic cells may consist of metal-semiconductor barriers rather than p-n junctions. The operation of a metal-semiconductor photovoltaic cell, or Schottky-barrier photovoltaic cell, will now be illustrated through the use of energy level diagrams. Figure 12 shows

a metal-semiconductor contact without bias and without illumination. This is the case for no current flow across the barrier. It is assumed that the barrier is high enough so that no electron interchange is permitted across the top of the barrier.

Figure 13 shows the same diode under illumination, with its terminals open-circuited. Since the diode has been open-circuited, no current can flow. The net result is the photovoltage V_f which is equal to the difference between the position of the Fermi level in the metal and the Fermi level in the semiconductor. The obvious cause of this photovoltage is the excitation of the electrons from the metal to the semiconductor.

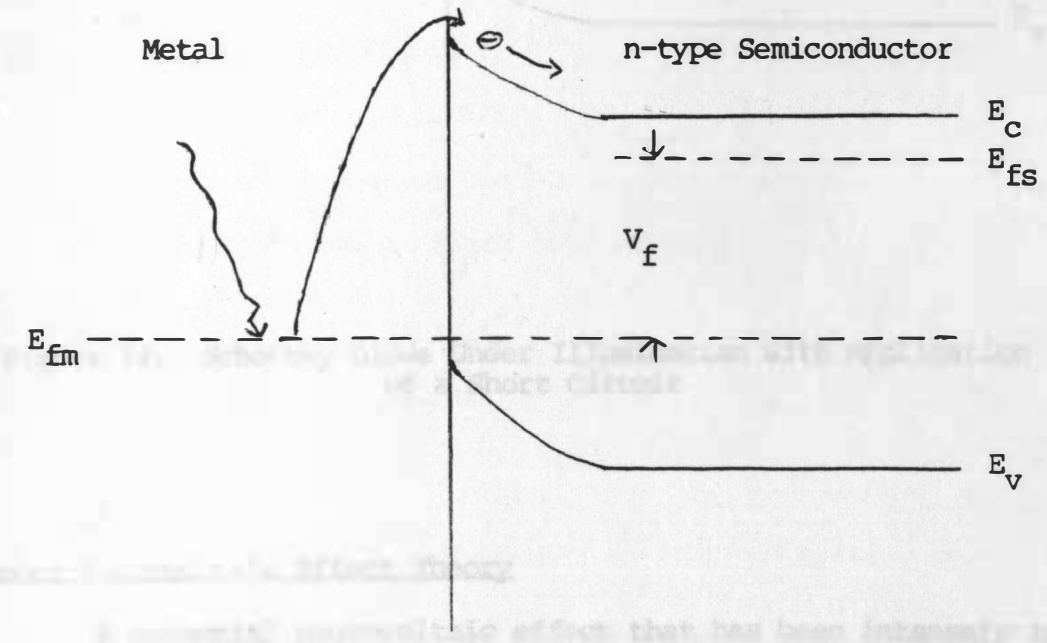


Figure 13. Schottky-barrier Diode Under Illumination with Its Terminals Open-circuited

An illuminated Schottky diode under the application of a short-circuit is shown in Figure 14. Under this condition maximum current is generated with zero voltage existing across the Schottky diode.

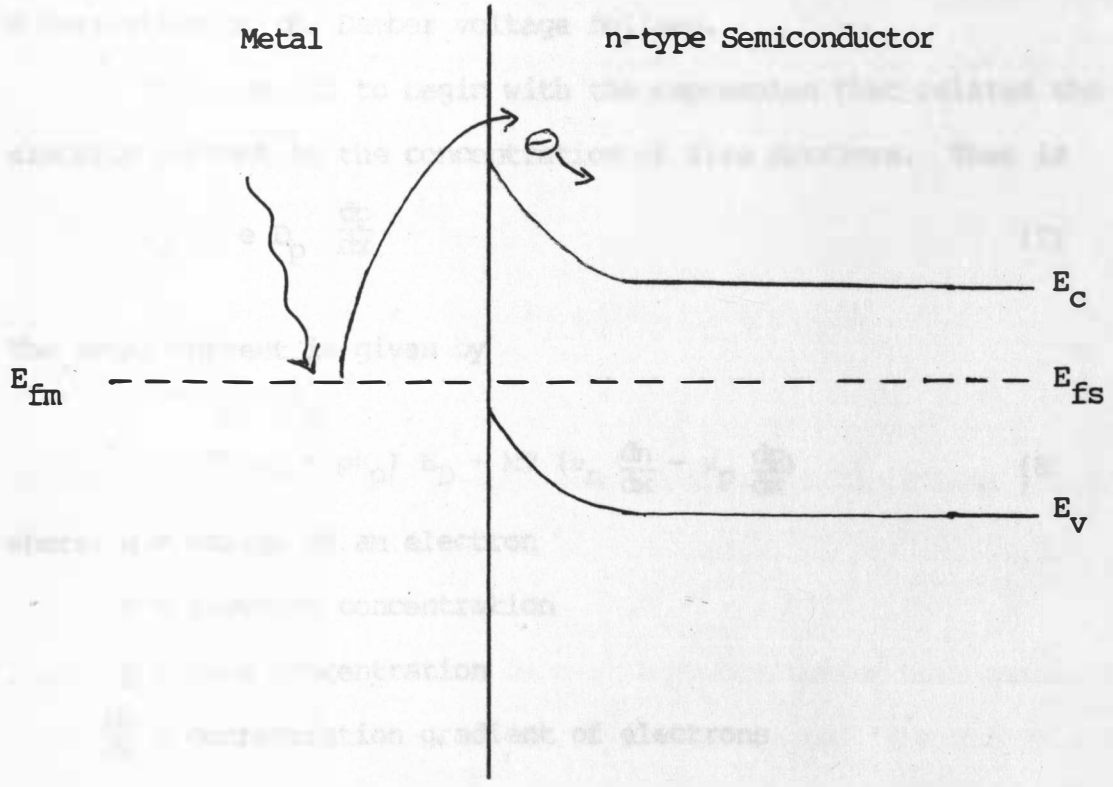


Figure 14. Schottky Diode Under Illumination with Application of a Short Circuit

Dember Photovoltaic Effect Theory

A potential photovoltaic effect that has been intensely investigated during this study is the Dember photovoltaic effect. The Dember effect occurs within the bulk of the semiconductor crystal.

Generally, it arises when one type of carrier (either electron or hole) predominates in the semiconducting crystal and is excited by radiation that is nonuniformly distributed.[9]

Myamlin and Pleskov[26] present a mathematical description of the Dember current and voltage. A summary of their results, including a derivation of the Dember voltage follows.

It is useful to begin with the expression that relates the electric current to the concentration of free carriers. That is

$$i_p = -e\, D_p \frac{dp}{dx} \tag{7}$$

The total current is given by

$$i = i_p + i_n$$

$$= q(n\mu_n + p\mu_p)\, E_D + kT\, (\mu_n \frac{dn}{dx} - \mu_p \frac{dp}{dx}) \tag{8}$$

where: q = charge of an electron

n = electron concentration

p = hole concentration

$\frac{dn}{dx}$ = concentration gradient of electrons

$\frac{dp}{dx}$ = concentration gradient of holes

k = Boltzmann's constant

T = temperature

μ_n = electron mobility

μ_p = hole mobility

E_D = Dember electric field

The total current equals zero for steady-state conditions with illumination. One can solve for the Dember electric field, E_D, by setting the total current in equation 8 equal to zero. This yields

$$E_D = \frac{-kT}{q} \frac{\mu_n \frac{dn}{dx} - \mu_p \frac{dp}{dx}}{n \mu_n + p \mu_p} \tag{9}$$

In the bulk of the material, usually several diffusion lengths, the concentration of excess carriers vanishes and $\Delta n = \Delta p$. Then $dp/dx = dn/dx$ and equation 9 can be rewritten in the form

$$E_D = \frac{-kT}{q} \frac{\mu_n - \mu_p}{n \mu_n + p \mu_p} \frac{dn}{dx} \tag{10}$$

Now, the bulk conductivity of the sample is given by,

$$\sigma_B = q(\mu_n n + \mu_p p) \tag{11}$$

Differentiating equation 11 with respect to the x-coordinate yields,

$$\frac{d\sigma B}{dx} = q (\mu_n + \mu_p) \frac{dn}{dx} \tag{12}$$

Equation 12 can be solved for dn/dx. By substituting this quantity into equation 10, the quantity dn/dx is eliminated. The Dember field becomes

$$E_D = \frac{-kT}{q} \frac{\mu_n - \mu_p}{(\mu_n + \mu_p) \sigma_B} \frac{d\sigma B}{dx} \tag{13}$$

The denominator of equation 13 was obtained through equation 11. Integrating equation 13 yields the potential difference that arises

$$V = -\int_{x=\infty}^{x=L} E_D \, dx = -\frac{kT}{q} \frac{\mu_n - \mu_p}{\mu_n + \mu_p} \ln \left(\frac{\sigma_{ill}}{\sigma_{B^O}}\right) \tag{14}$$

where σ_B^o is the dark conductivity of the sample and is given by

$$\sigma_B^o = q\,(\mu_n n^o + \mu_p p^o) \tag{15}$$

The conductivity of the sample at the point $x = L_1$ under illumination is given by

$$\sigma_{ill} = \sigma_B^o + \Delta\sigma \tag{16}$$

Substitution of equations 15 and 16 into equation 14 yields,

$$V_D = \frac{kT}{q}\,\frac{\mu_p - \mu_n}{\mu_n + \mu_p}\,\ln\left(1 + \frac{\Delta\sigma}{\sigma_B^o}\right) \tag{17}$$

which simplifies to

$$V_D = \frac{kT}{q}\,\frac{\mu_p - \mu_n}{\mu_n + \mu_p}\,\frac{\Delta\sigma}{\sigma_B^o} \tag{18}$$

for the case when $\Delta\sigma \ll \sigma_B^o$.

Pankove[30] uses a similar argument and arrives at a similar expression for the Dember voltage given by

$$V_D = \frac{kT}{q}\,\frac{b-1}{b+1}\,\ln\left[1 + \frac{(b+1)\,\Delta n}{bn_o + p_o}\right] \tag{19}$$

In the absence of conductivity data, equation 19 tends to be a somewhat more useable expression. Here b is the ratio of the highest to lowest mobilities. If the mobilities of electrons and holes are equal, then b = 1 and the Dember photovoltage is zero. Usually the mobility of the electrons is greater than that of the holes and the Dember voltage is not much greater than kT/q.

The Dember voltage tends to be independent of other effects that may occur at a surface barrier. It is viewed as an additional component which may add or subtract from the photovoltage generated at the barrier.

EXPERIMENTAL METHODS AND ANALYSIS TECHNIQUES

The crystals used in this investigation were previously prepared by investigators at South Dakota State University[3] and at Oklahoma State University.[18] All the crystals used were prepared by the flux method of crystal growth. A flux is a material which lowers the melting point of the substance with which it is mixed. The flux method of crystal growth is one in which the crystals are grown from a supersaturated solution. That is, the solution contains more of the solute than it can hold in equilibrium with the solid. The particular solution that was used for the crystal growth was a mixture of two parts of Cu_2O to one part SnO_2. This solution was then placed in a furnace and heated to a temperature of approximately 1100-1300^{o}C. This temperature was maintained for several hours, and then decreased a few degrees every hour.

Five different crystals were used in this investigation, each approximately 1-3mm in length. They will be referred to by number (1,2,3,4,5). Crystals 1-4 had not undergone any type of treatment previously. Crystal 5 had a pink color initially which is probably due to excessive oxygen exposure during the growth process. The other crystals were transparent. Some of the crystals used contained black veins. These veins were probably due to cuprous oxide entrapped during the growth process. However, after several cleanings these black veins were removed from all but crystal 5.

The crystals were cleaned using an aqua regia solution each time before they were used. Aqua regia consists of a mixture of

approximately two parts HCl and one part HNO_3. The cleaning procedure consisted of an approximate 2-3 hour bath in aqua regia, followed by a 20 minute rinse in acetone, and finally a 10 minute rinse in methanol. The crystals were stored in methanol until ready for use.

The sample holder that was used in this investigation is diagrammed in Figure 15. It consists of a quartz tube with an adjustable quartz inner tube in which the crystal was placed. The crystal was secured between two platinum electrodes. One end of the quartz tube remained stationary while the other end was adjustable. This allowed for more accurate placement of the crystal between the electrodes. The electrodes were always cleaned with acetone before the crystal was positioned in the sample holder. The ends of each crystal were sanded as smoothly as possible to allow for better contact with the electrodes. The sample was placed in the holder with the long axis (c-axis) perpendicular to the direction of the light. A sliding black shield was fitted to the exterior of the sample holder. Thus the amount of light striking the crystal could be regulated. The black shield was used because according to the Dember theory, the crystals should be partially illuminated. The sample holder was mounted between two metal stands and was then connected to a digital voltmeter as shown in Figure 16. A mercury lamp was used which emits ultraviolet light. This was chosen because its energy is close to the band gap energy of SnO_2. The lamp was covered with a black shield, except for a small portion which was directed onto the crystal.

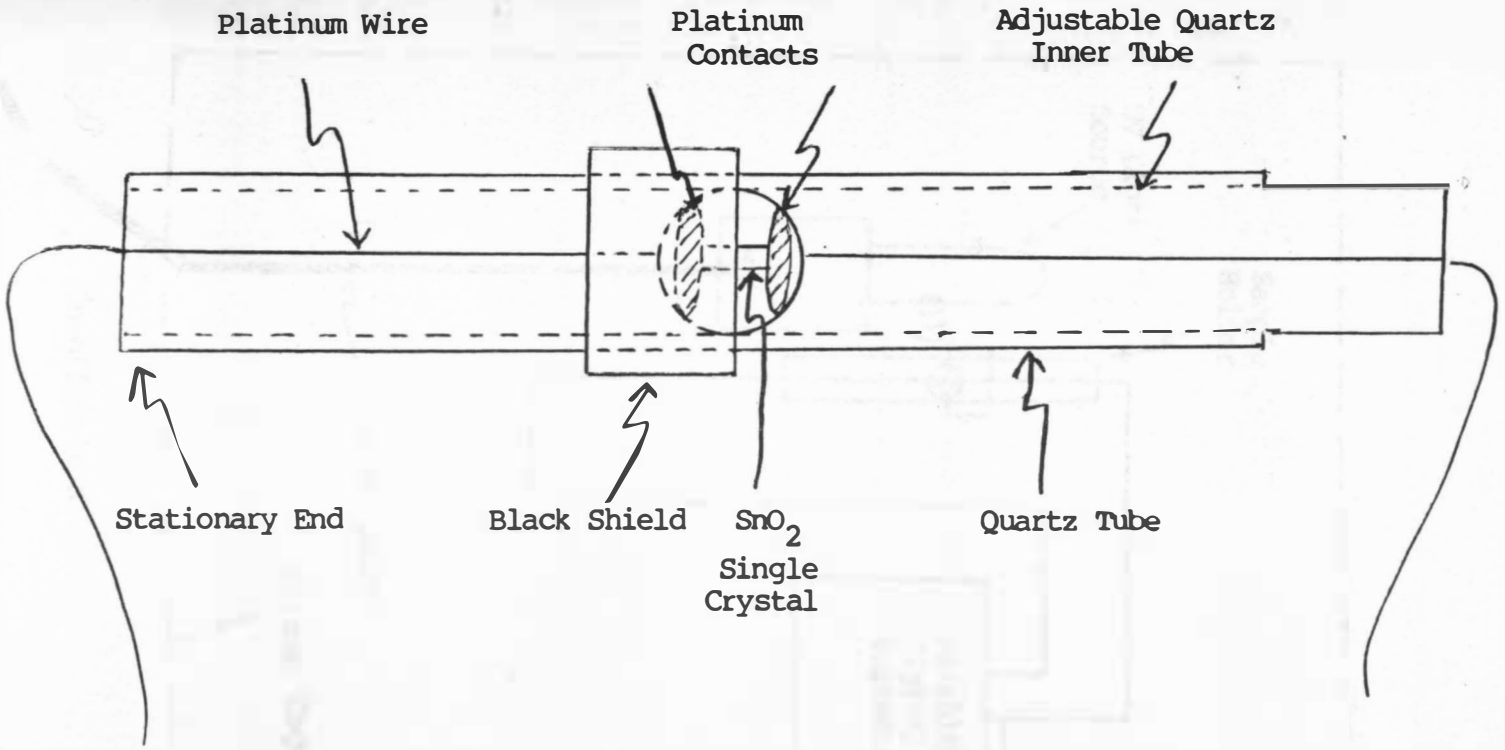


Figure 15. The SnO_2 Sample Holder

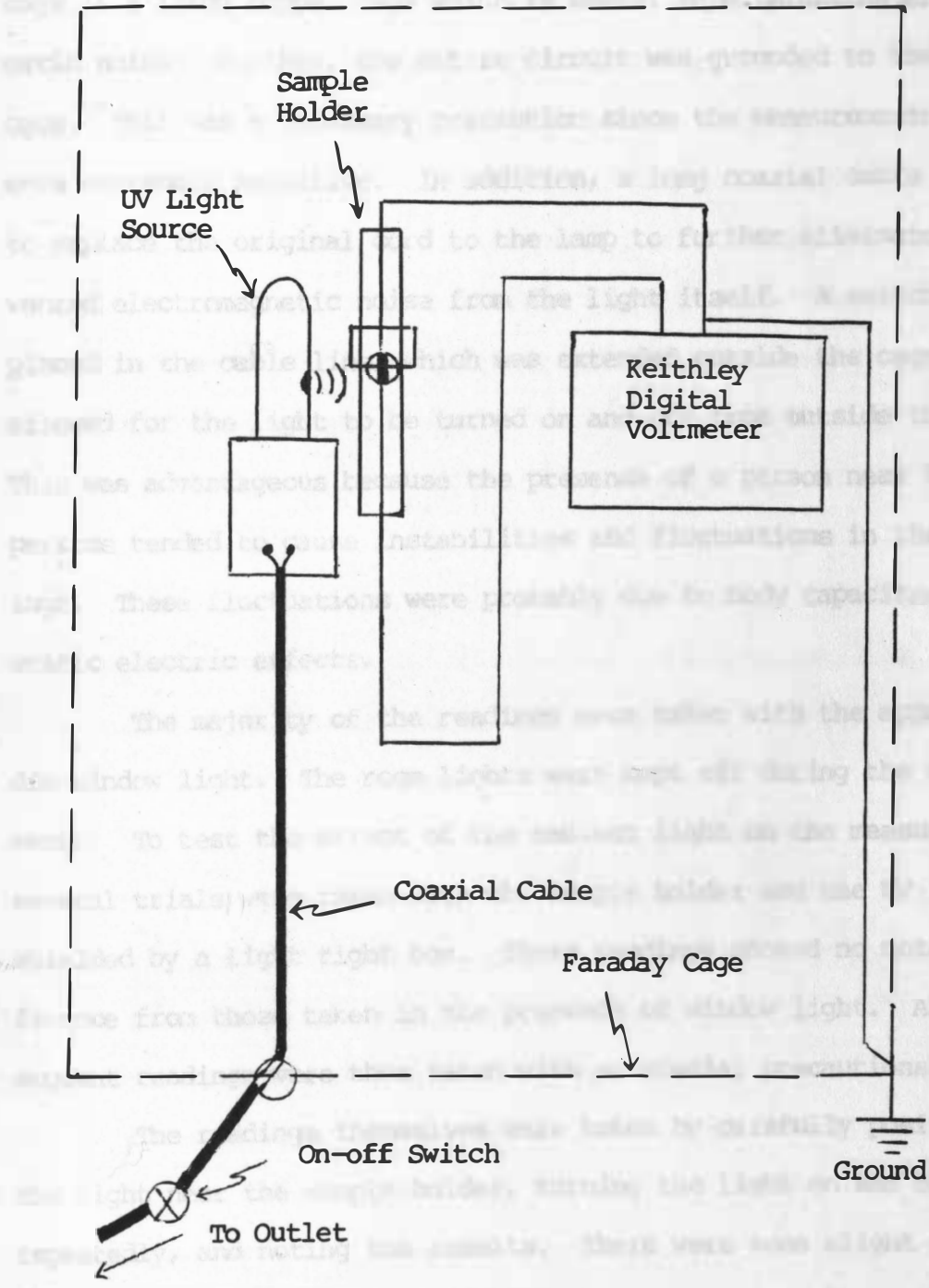


Figure 16. Schematic Diagram of Experimental Apparatus

The experiment was conducted inside a Faraday cage. A Faraday cage is a large copper cage which is useful in eliminating electromagnetic noise. Further, the entire circuit was grounded to the Faraday cage. This was a necessary precaution since the measurements sought were extremely sensitive. In addition, a long coaxial cable was used to replace the original cord to the lamp to further eliminate any unwanted electromagnetic noise from the light itself. A switch was placed in the cable line, which was extended outside the cage. This allowed for the light to be turned on and off from outside the cage. This was advantageous because the presence of a person near the apparatus tended to cause instabilities and fluctuations in the readings. These fluctuations were probably due to body capacitance or static electric effects.

The majority of the readings were taken with the apparatus in dim window light. The room lights were kept off during the measurements. To test the effect of the ambient light on the measurements, several trials were taken with the sample holder and the UV light shielded by a light tight box. These readings showed no notable difference from those taken in the presence of window light. All subsequent readings were thus taken with no special precautions.

The readings themselves were taken by carefully positioning the light near the sample holder, turning the light on and off repeatedly, and noting the results. There were some slight effects due to the switch itself, but these were generally quite neglible. Careful positioning of the crystal in the sample holder is crucial.

Relative humidity values were monitored each day a measurement was taken. This was done since most of the readings were taken during the summer months when the relative humidity may be high. There was concern that excessive humidity might cause a buildup of monolayers of water on the surface of the crystal, increasing the potential barrier. Further, these monolayers of water could then prevent the escape of electrons to or from the crystal which would result in a decrease in observed effects. Two silica drying gel containers were obtained and used each time measurements were taken under the light tight box. There were no noticeable changes in the readings when the silica gel was used.

After several measurements were taken on the untreated crystals, crystal 4 was randomly selected for heat treatments in both oxygen (air) and nitrogen atmospheres. Heating the crystal has the effect of "fixing" the particular treatment.

For the treatments in oxygen, the crystal was placed inside a quartz tube which was then inserted into a furnace. The furnace was calibrated using a resistance thermometer bridge. The crystal was treated for 3 hours at a temperature of approximately 600^{o}C. The quartz tube and crystal were rapidly removed from the furnace in order that proper quenching of the crystal could occur. After heating, the crystal was a slightly pink color. A series of measurements were then taken on the oxygen heat treated crystal.

After measurements were taken with the treated crystal, it was heat treated in a nitrogen atmosphere. The experimental apparatus for the nitrogen heat treatment is shown in Figure 17. The crystal was placed inside a gas-exchange chamber. This apparatus was connected to a vacuum pump and to a nitrogen supply, as shown in the diagram. The vacuum pump was used to evacuate the air from the chamber. Then a positive pressure of about 2-3 psi of nitrogen was supplied to the chamber during the heating process. During this process, the crystal and gas-exchange apparatus were placed inside the furnace. The crystal was heated for 3 hours at a temperature of approximately 770^{o}C. After heating the crystal was again removed immediately from the furnace to promote rapid quenching.

It should be noted that the length of heating time and the temperatures used were somewhat randomly chosen. This was done with the intent to discover just how long and at what temperature the crystals must be heated to either increase or decrease the potential barrier at the surface of the sample. Thus, different heating times were investigated. The choice of temperature is not as crucial.

After heat treating the crystal in nitrogen it was observed that the crystal had returned to its original clear state. Again, a series of measurements were taken with this crystal before any further treatments were performed.

Following the nitrogen treatment, the crystal was again heat treated in an oxygen atmosphere. However, the treatment time was reduced to 20 minutes at approximately 600^{o}C. This was done, in part,

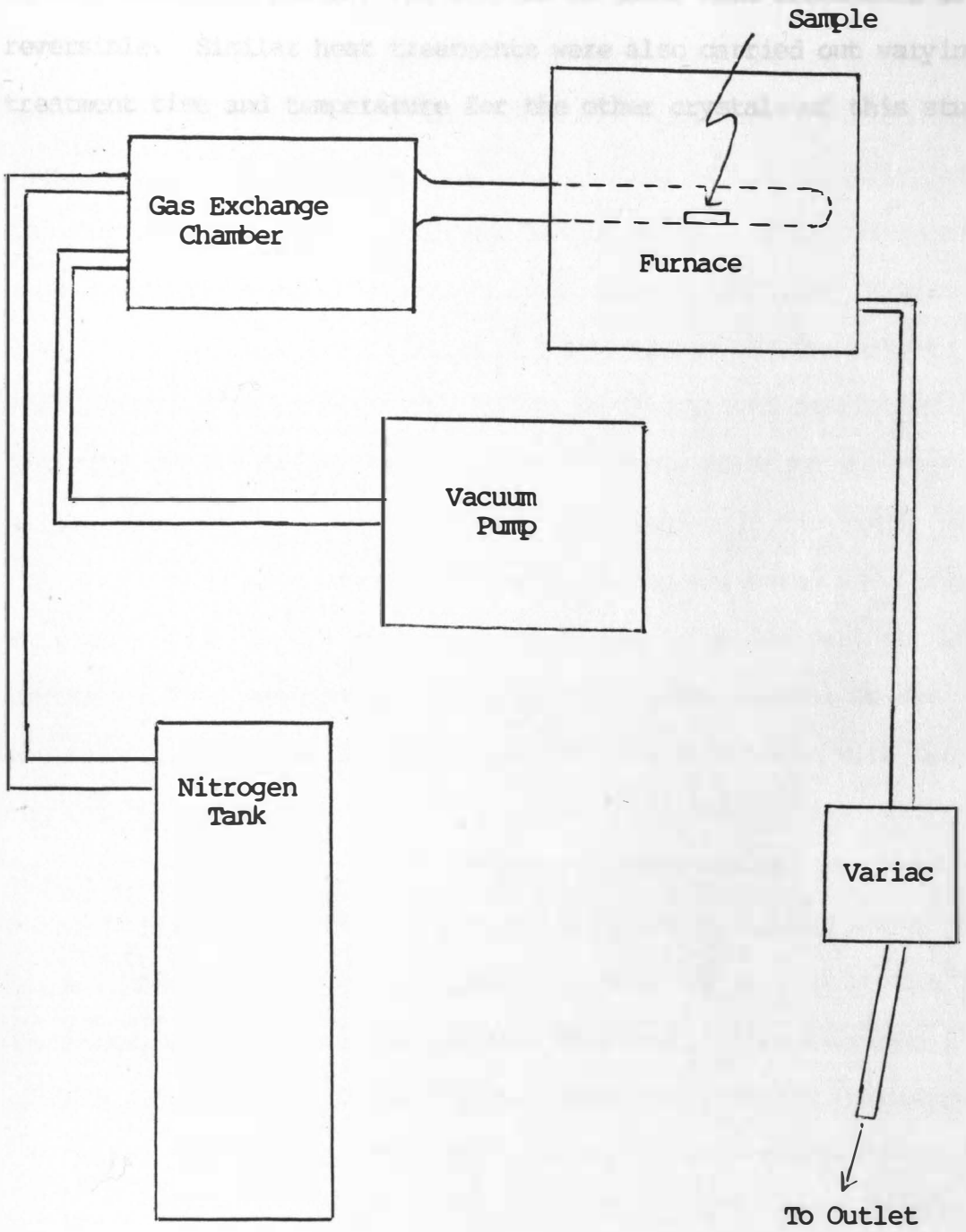


Figure 17. Schematic Diagram of Crystal Heat-treatment Apparatus

to help determine whether the effects of these heat treatments are reversible. Similar heat treatments were also carried out varying treatment time and temperature for the other crystals of this study.

RESULTS

The first objective of this investigation was to prove the existence of a photovoltaic effect in stannic oxide with platinum contacts. Crystal 2 was chosen for this task as it was slightly larger and thus easier to position in the sample holder. A number of trials were taken with this crystal partially illuminated. The results of these trials showed a mean value of photovoltage varying between 0.1 and 1.0 mV, as shown in Table 1. The results proved consistent which indicates that a definite effect was observed, although the magnitude varied considerably with the crystal positioning in the sample holder.

Most of the measurements taken on the untreated SnO_2 crystals were taken with partial illumination of the light incident on the crystals. This was done in accordance with the original Dember photovoltaic theory. However, readings were also taken with the crystal totally exposed to the light to test this assumption. The results for total exposure showed no significant photovoltages produced. Further, readings taken with the crystal totally exposed would fluctuate, sometimes very wildly. However, with the crystal partially illuminated, very stable readings were obtained. These readings indicated a possible bulk photovoltaic effect, such as that described in the Dember theory. However, this does not eliminate a possible contribution due to the Schottky effect. The unstable readings could be explained by equal and opposite photovoltages being produced at the contacts which may cancel the expected effect.

Table 1. Mean Photovoltages for Untreated Crystal 2

Number of Trials	Mean Photovoltage (mV)	Standard Deviation (1σ)
8	0.6	0.4
5	0.9	0.3
7	0.1	0.1
10	0.2	0.1
13	0.1	0.1
10	0.8	0.3
11	1.0	0.4
10	0.7	0.4
15	0.8	0.2
12	0.4	0.4
6	0.5	0.4
12	0.4	0.3
6	0.1	0.1

On days when the relative humidity was very high (>90%) no significant values were measured. This failure was attributed to excessive monolayers of water which collected on the surface of the crystal. Thus, data was collected on days when the relative humidity ranged from approximately 40 to 70%.

The results for these untreated crystals show photovoltages in the 0.1 to 2.0 mV range. Similar results were obtained for crystals 1, 2, 3, and 4, as shown in Table 2. However, no significant results were obtained with crystal 5. This was due to the fact that crystal 5 had been previously exposed to oxygen during the growth process. As the results that follow show, no significant data is found for a crystal which has been heat treated in an oxygen atmosphere. Further, after several cleanings in aqua regia, crystal 5 still maintained a black streak which indicates the presence of cuprous oxide inclusions. After treatment in nitrogen for several hours, the crystal still displayed a pink color. This is most likely due to an excess of chromium impurities.[40]

A portion of this investigation dealt with determining the effects of various heat treatments on the observed photovoltage. Two types of heat treatments were studied in this investigation: (1) heat treatment in an oxygen atmosphere and (2) heat treatment in a nitrogen atmosphere.

An additional part of this investigation was to determine whether or not these heat treatment effects were reversible. In order to do this, alternate oxgyen/nitrogen heat treatments on various

Table 2. Summary of Results for Untreated Crystals

Crystal Number	Number of Trials	Mean Photovoltage (mV)	Standard Deviation (1σ)
4	11	0.3	0.2
4	22	0.4	0.3
4	24	0.6	0.3
4	24	0.3	0.1
4	24	0.2	0.1
1	12	0.2	0.1
1	24	0.6	0.1
2	12	0.6	0.2
2	12	0.2	0.1
2	12	0.3	0.1
4	12	0.4	0.1
4	12	0.6	0.2
3	12	0.5	0.2
3	12	0.8	0.1
2	5	1.7	0.5
2	12	1.2	0.2
2	7	1.4	0.3
1	7	0.8	0.1
1	12	0.8	0.2
3	24	0.2	0.1
2	12	0.1	0.1
2	12	1.0	0.5
2	11	0.2	0.1
2	12	0.3	0.1
2	6	0.1	0.1

crystals were studied. Crystal 4 was randomly selected to undergo the initial heat treatments in both the oxygen and nitrogen atmospheres. The results of these various treatments on crystal 4 are shown in Table 3. Photovoltages in the 0.5 mV range were observed with this crystal before any treatments were begun. The crystal was initially treated in air for 3 hours at a temperature of about 600°C. After this treatment the crystal took on a pink color from the changing of Cr^{2+} into Cr^{3+} due to electrons being captured by the near surface oxygen.[40] Readings then taken with this treated crystal resulted in no significant observed photovoltages.

The sample was then heat treated in a nitrogen atmosphere for 3 hours at a temperature of approximately 770°C. Results of the measurements taken after this treatment indicate significant photovoltages varying between 0.2 and 2.4 mV. Again each trial, which represents a repositioning of the sample, gives wide variations in magnitude for the observed photovoltages.

To determine if the oxygen/nitrogen heat treatments were reversible, crystal 4 was heat treated in an oxygen atmosphere for 20 minutes at a temperature of approximately 600°C. The crystal again displayed a pink color. Subsequent measurements reveal no significant photovoltages were produced. The data indicates a treatment time of 20 minutes produces the same effect as a treatment time of 3 hours. The data further supports the reversibility of these heat treatment effects.

Table 3. Heat Treatment Data for Crystal 4

Type of Treatment	Length of Treatment (min.)	Treatment Temperature (^{o}C)	Number of Trials	Mean Photovoltage (mV)	Standard Deviation (1σ)
Oxygen	180	600	12	0.0	0.1
Oxygen	180	600	12	0.0	0.1
Nitrogen	180	770	11	0.2	0.1
Nitrogen	180	770	11	0.4	0.2
Nitrogen	180	770	10	0.2	0.2
Nitrogen	180	770	10	0.2	0.1
Nitrogen	180	770	11	0.2	0.1
Nitrogen	180	770	13	0.2	0.2
Nitrogen	180	770	12	1.4	0.3
Nitrogen	180	770	12	1.1	0.1
Nitrogen	180	770	12	1.1	0.1
Nitrogen	180	770	12	0.2	0.1
Nitrogen	180	770	12	0.9	0.5
Nitrogen	180	770	12	2.4	0.4
Nitrogen	180	770	12	1.7	0.5
Nitrogen	180	770	11	1.4	0.5
Oxygen	20	600	12	0.1	0.1
Oxygen	20	600	12	0.1	0.1
Oxygen	20	600	12	0.0	0.1
Oxygen	20	600	12	0.0	0.1
Oxygen	20	600	12	0.0	0.1
Oxygen	20	600	12	0.0	0.1
Oxygen	20	600	12	0.0	0.1

Crystal 2 was chosen to further test the effects of heat treatments in oxygen and nitrogen atmospheres. The results of various treatments are given in Table 4. The data shows that a treatment time of 3 hours in oxygen at a temperature of approximately 770^{o}C results in no significant photovoltages.

The temperature was lowered to 500^{o}C for the treatment in nitrogen. This was done to test the effect of temperature on the treatment process. The data shows no significant photovoltages produced when crystal 2 was treated in nitrogen at 500^{o}C for 10 minutes or for 30 minutes. When the treatment time was extended to 50 minutes the data indicates significant photovoltages were produced.

To further verify the reversibility of these heat treatments in alternate oxygen/nitrogen atmospheres crystal 2 was again treated in oxygen for 60 minutes at 500^{o}C. After treatment no significant photovoltages were produced as shown in Table 4. Thus alternate heat treatment effects in oxygen and nitrogen are reversible.

Table 4. Heat Treatment Data for Crystal 2

Type of Treatment	Length of Treatment (min.)	Treatment Temperature (^{O}C)	Number of Trials	Mean Photovoltage (mV)	Standard Deviation (1σ)
Oxygen	180	770	12	0.1	0.1
Oxygen	180	770	12	0.1	0.1
Oxygen	180	770	12	0.1	0.1
Oxygen	180	770	12	0.1	0.1
Nitrogen	10	500	11	0.1	0.1
Nitrogen	10	500	11	0.1	0.1
Nitrogen	10	500	11	0.1	0.1
Nitrogen	10	500	11	0.0	0.1
Nitrogen	30	500	12	0.1	0.1
Nitrogen	30	500	12	0.1	0.1
Nitrogen	50	500	10	0.3	0.1
Nitrogen	50	500	10	0.1	0.1
Nitrogen	50	500	10	0.2	0.1
Oxygen	60	500	11	0.0	0.1
Oxygen	60	500	11	0.0	0.1
Oxygen	60	500	11	0.0	0.1

CONCLUSIONS

Results of this investigation verify the existence of a photovoltaic effect in stannic oxide single crystals with platinum contacts. The data indicates photovoltages varying from 0.0 to 2.4 mV depending on prior heat treatments in oxygen and nitrogen atmospheres. Crystal heat treatment in an oxygen atmosphere gave no significant photovoltages. Crystal heat treatment in a nitrogen atmosphere gave photovoltages in the 1.0 to 2.4 mV range. Alternating these oxygen/nitrogen treatments demonstrated reversibility in these effects.

The most probable explanation of these effects is a Schottky barrier created by the platinum/stannic oxide interface of the crystal. This would explain the variation in photovoltage with heat treatments since the surface potential barrier can be modified in that manner. An increase of the barrier height from oxygen adsorption could very easily explain the disappearance of the photovoltage since the barrier energy could be raised above the metal Fermi energy by an amount greater than the photon energies. The results of nitrogen treatment can be explained since it decreases the surface potential barrier and allows electron excitation over the surface potential barrier.

The variation in photovoltage with the repositioning of the crystal also supports the above explanation. Each time the crystal position is changed the contact conditions are changed drastically and thus the excitation of electrons will be affected together with the

associated contact resistance. Although results of this study do not rule out a possible contribution due to the Dember effect, they do suggest that it cannot be the major factor. It would be highly improbable for a bulk effect to show the observed heat treatment effects and positioning effects since no such results have been reported in the past.

SUGGESTIONS FOR FURTHER STUDY

It is suggested that this study be extended to allow for simultaneous heat-treatment, illumination of the crystals, and measurement of the photovoltaic effect. In order to do this a more elaborate gas-exchange chamber must be built. A special furnace would be needed to allow for exposure of the crystal to the light source while it is being heated. This type of apparatus would allow the measurement of the photovoltaic effect while the heat-treatment is being carried out.

Further, it is suggested that the above mentioned equipment be used in conjunction with heat-treatments in other atmospheres, such as helium and hydrogen. It is suggested that light of different wavelengths be used for illumination of the crystals. This could be achieved through the use of a monochromator or tunable laser. In addition, this would allow one to study how heat treatment affects the wavelength at which the photovoltaic effect can be observed. In that manner, it may be possible to measure the change in the surface potential barrier with heat treatment.

LITERATURE CITED

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